

INCONSISTENCIES IN DEW POINTS FROM DIFFERENT ALGORITHM TYPES POSSIBLE CAUSES AND SOLUTIONS

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ABSTRACT

Calculations of natural gas dew points are quite important in the gas processing industry. A number of software packages used by the industry have multiple options for calculations of dew points. One option is to fix the pressure and the software will calculate the dew point temperature. Another option is to have the software generate the phase envelope for the natural gas mixture. A third option is for the user to perform flash calculations at a fixed pressure and varying temperatures until the amount of condensed liquid is arbitrarily small. Sometimes, these three different options yield three different calculated dew points. Because the three different dew point options involve nested iterative loops which solve for liquid and vapor densities and component fugacities as well as the temperature or vapor fraction, the three options should agree within some measure of the different convergence criteria used by the three options, provided the methodology used in a given option does not fail. Examples of dew point calculation differences by the three options are presented and some analysis of which option best represents the equation of state used is given. In addition, possible methods for reducing the inconsistencies are discussed.

INTRODUCTION

The focus of this paper is on the need for improvements in process simulator equation of state vapor-liquid equilibrium algorithms for natural gas mixtures containing large numbers of heavy hydrocarbons. Calculation results are presented for two commonly used simulators to show that each simulator calculates inconsistent dew points using different calculation options available in each simulator. Possible causes for these inconsistencies as well as possible solutions are discussed to encourage reductions in these inconsistencies in future versions of process simulators.

INCONSISTENCIES USING SIMULATOR NO. 1

An example of inconsistencies in dew points calculated using different algorithm types is given here for the natural gas mixture composition in Table 1. The components with an asterisk (C6*, C7*, etc.) are pseudo-components for which the characterization parameters given in Table 1 have been used in the calculations.

Calculations were performed using two simulators commonly utilized by engineers in gas processing. The Peng-Robinson equation of state was used for the calculations. First the phase envelope option was used to calculate temperature-pressure conditions of bubble points and dew points on the phase envelope of the mixture in Table 1. Then a dew point condition on the phase envelope near 40 bar absolute pressure was selected. For Simulator No. 1, this pressure was 41.0 bar(a) and the phase envelope generated dew point temperature was 52.59°C, as shown in Table 2. Then a separator module calculation was performed using the composition in Table 1 for the feed stream and specifying the separator condition to be 41.0 bar(a) and ratio of the moles of vapor to moles of feed, V , to be 1.0. The resultant dew point temperature, shown in Table 2 was 50.17°C. Finally, isothermal-isobaric flash calculations were performed using the

composition in Table 1 at a fixed pressure of 41.0 bar(a) and temperatures starting with 52.59°C and successively reducing the temperature until the calculated moles of liquid to moles of feed, L , was nonzero. By this procedure, the dew point from the isothermal-isobaric flash calculations was interpreted to be 41.57°C, as shown in Table 2.

The results in Table 2 for Simulator No. 1 demonstrate the large inconsistencies in calculated dew points for natural gas mixtures that can occur using different simulator computation modules. Consider the following scenario. Suppose a gas processing plant has been designed using Simulator No. 1 with the Peng-Robinson equation of state. Assuming the dew point from the isothermal-isobaric flash calculation is the most accurate dew point in Table 2, and then if the design final two phase condition temperature-pressure of the process stream were 41.0 bar(a) and 41.57°C, the sales gas would be totally vapor at 41.0 bar(a) for any temperature above 41.57°C.

Consider that the contract sales gas dew point specification states that at 41.0 bar(a) no liquid can form so long as the temperature is above 42.00°C. If in the actual operating gas processing plant the sales gas is the vapor stream from a separator at 41.0 bar(a) and 41.57°C, with the composition in Table 1, then this gas will meet the dew point specification, provided there is no liquid carryover. On the other hand, if the gas purchaser uses the phase envelope module in Simulator No. 1 with the Peng-Robinson equation of state, a dew point temperature of 52.59°C will be calculated at 41.0 bar (a). If the gas purchaser believes the phase envelope generator to be correct, the purchaser will believe the purchased natural gas does not meet specifications and the gas dew point is 10°C greater than the contract dew point. Differences of this sort can cause contractual disputes and can be serious issues of contention in litigation involving gas quality.

INCONSISTENCIES USING SIMULATOR NO. 2

The results in Table 3 were obtained using Simulator No. 2 to calculate dew points for the mixture composition in Table 1 at 39.93 bar(a).

For Simulator No. 2, the phase envelope calculation indicated a dew point temperature of 55.00°C at 39.93 bar(a). The separator calculation at 39.93 bar(a) with the ratio of the moles of vapor to moles of feed, V , specified to be 1.0 yielded a dew point temperature of 42.24°C. Thus, a disagreement of more than 12°C occurs using these different calculation modules in Simulator No. 2. When isothermal-isobaric flashes at 39.93 bar(a) were performed using Simulator No. 2, starting at 55.00°C and decreasing the temperature in 0.4°C increments, the calculations indicated no liquid present until the temperature was below 41.00°C. Isothermal-isobaric flashes at 39.93 bar(a) then were performed starting at 41.00°C and increasing the temperature in 0.4°C increments. These calculations indicated that liquid was present at temperatures where the previous flashes using decreasing temperature indicated no liquid present. These results tend to indicate that the isothermal-isobaric flash algorithm used in Simulator No. 2 uses the vapor-liquid split obtained in the most recent flash as the initial value for the iterative steps in the current flash and further that the Gibbs free energy has not been used to perform a stability analysis to determine if the mixture is more stable as a single phase or a two phase system. Issues related to initial values of iteration variables and stability analysis is discussed in more detail in a later section.

VLE USING EQUATIONS OF STATE

Vapor-liquid equilibrium (VLE) calculations using equations of state must satisfy the following so called condition equations, which can be derived from classical thermodynamics,

$$T^V = T^L \tag{1}$$

$$P^V = P^L \quad (2)$$

$$\bar{f}_i^V = \bar{f}_i^L \quad (3)$$

where the superscripts V and L refer to the vapor and liquid phases, respectively. To satisfy these condition equations it is necessary to calculate the fugacity of the i th component, \bar{f}_i , in both vapor and liquid phases. The fugacity of the i th component in a fluid mixture, \bar{f}_i , is related to the equation of state by the following relation,

$$RT \ln \left[\frac{\bar{f}_i / x_i}{rRT} \right] = \int_0^r \left[r \left(\frac{\partial PV}{\partial n_i} \right)_{T,V,n_i \neq i} - rRT \right] \frac{dp}{r^2} \quad (4)$$

In equation 4, x_i is the mole fraction of the i th component in the mixture, which may be either liquid or vapor; V is the volume of the phase. When the mixture equation of state expression for the absolute pressure P as a function of absolute temperature T , molar density r and phase component mole fractions x_i is used in Equation (4), the equation of state expression for the component fugacity \bar{f}_i in the phase results.

Isothermal-isobaric flash calculations as well as dew point and bubble point calculations also must satisfy the following relation that can be derived from the mole balance relations for each component (vapor moles plus liquid moles equal total moles),

$$F(T, P, V) = \sum_{i=1} \frac{z_i(1 - K_i)}{K_i V + (1 - V)} \quad (5)$$

In this relation z_i is the mole fraction of the i th component in the feed mixture. At vapor-liquid equilibrium, one mole of the feed mixture splits into V moles of vapor and $(1 - V) = L$ moles of liquid. The equilibrium vaporization ratio or K -value for the i th

component, K_i , is the ratio of y_i and x_i , the equilibrium mole fractions of the i th component in the vapor and liquid phases respectively,

$$K_i = \left(\frac{y_i}{x_i} \right) \text{ equilibrium} \quad (6)$$

For one mole of feed mixture, the number of moles of the i th component in the feed, vapor and liquid are x_i , $y_i V$ and $x_i(1 - V)$, respectively, that is,

$$z_i = y_i V + x_i(1 - V) \quad (7)$$

when z_i , K_i and V have been determined y_i and x_i can be solved using Equations 6 and 7.

In dew point, bubble point and isothermal-isobaric flash calculations, two of the three quantities T , P and V are specified and the third is searched for. In isothermal-isobaric flash calculations, T and P are specified and V is sought. In dew point calculations, $V = 1$ is specified and either P or T is sought. Similarly, in bubble point calculations, $V = 0$ is specified and P or T is sought. Other problems may specify values of V between 0 and 1. In all cases, the solution for the unknown whether $(T, P, \text{or } V)$ is that value of the unknown for which $F(T, P, V) = 0$ in Equation 5.

If the K -values (K_i) in Equation 5 were functions only of temperature and pressure, virtually any iterative search method will converge to the solution for the unknown $(T, P, \text{or } V)$. For example, if T and P are fixed, and K_i are known then the flash calculation is an iterative search for V in the range 0 to 1.

When the equation of state method is used for mixture vapor-liquid equilibrium prediction, the condition equation $\bar{f}_i^V = \bar{f}_i^L$, Equation 3, imposes an additional requirement that must be satisfied. The direct substitution method, discussed below, is a popular method for

simultaneously satisfying Equations 1, 2, 3 and 5 in isothermal-isobaric flash calculations using equations of state.

DIRECT SUBSTITUTION FLASH PROCEDURE

The essence of the direct substitution procedure is to directly substitute the current estimates of the K -values into Equation 5, solution of which leads to new vapor and liquid compositions which in turn are used in Equation 4 to calculate new fugacity values for each component in each phase, leading to new estimates for the component K -values.

The first step in the procedure is to perform a flash calculation for the feed mixture composition using first estimates of the K -values, denoted by R_i . The flash calculation yields the vapor-liquid split (V and L) and the component mole fractions, y_i , for the vapor phase and x_i , for the liquid phase. This allows calculation of the densities of the vapor and liquid phases using the equation of state. The composition and densities are then used to calculate component fugacities in each phase, using Equation 4. If the vapor fugacity of any component is different from its liquid fugacity, the ratio R_i in Equation 8 can be used as a new estimate for the K -value of the i th component in a new solution of Equation 5,

$$R_i = \frac{\bar{f}_i^L / x_i}{\bar{f}_i^V / y_i} \quad (8)$$

This cycle is repeated until the thermodynamic condition for equilibrium (equality of component fugacities in each phase) is satisfied, for then R_i in Equation 8 equals the equilibrium ratio, K_i in Equation 6. By this method, with the convergence criterion $i = 1, 2, N$,

$$\left| 1 - \bar{f}_i^V / \bar{f}_i^L \right| < EPSF \quad (9)$$

The direct substitution method generally converges provided the temperature-pressure condition is within the two-phase region (according to the equation of state utilized) and a two phase vapor-liquid split is obtained with the initial estimates of the component K -values. Michelsen [1] has given a mathematical description of the conditions under which convergence of the direct substitution method is assured.

For mixtures with large numbers of components, such as natural gas mixture compositions from extended chromatographic analysis, the direct substitution method often requires large numbers of iterations near high-pressure dew points and in the vicinity of the critical point. Various acceleration methods have been used to reduce the number of iterations required, but as noted by Michelsen [1] these methods can fail if the initial estimates of the K -values are too far from the solution values. For this reason, Michelsen [1] uses stability analysis, as an initial step to determine if the Gibbs free energy indicates the mixture at the $T - P$ condition is more stable as a two phase system or a single phase system. To determine if two phases are more stable than a single phase vapor at a given T-P condition, component feed mole fractions, z_i can be used to calculate vapor fugacities, \bar{f}_i^v . Then the initial estimates for K -values, R_i , can be used to estimate liquid compositions $x_i = z_i/R_i$ for calculations of liquid fugacities, \bar{f}_i^L . The K -value estimates then can be revised using

$$R_i = \frac{\bar{f}_i^L / x_i}{\bar{f}_i^v / z_i} \quad (10)$$

from which new values of x_i can be obtained. This iterative procedure can be continued until the convergence criterion in Equation 9 is satisfied. If the molar Gibbs free energy of the liquid composition is less than the molar Gibbs free energy of the vapor composition, the system is

more stable as a two phase rather than a single phase system. This stability test works effectively near dew points and far into the two phase region. The procedure can be modified by using the feed mole fractions z_i for calculation of liquid phase fugacities \bar{f}_i^L to determine if two phases are more stable than a single phase liquid at the T-P condition. For a two phase system, stability analysis also generates good initial estimates for K -values that Michelsen [2] uses in second order convergence methods in flash calculations leading to rapid solutions at high pressures and near the critical point. Based on Michelsen's [1,2] work, it is probable that when a simulator $T - P$ flash calculation yields a single phase (trivial solution) when there actually are two phases, the simulator has not used stability analysis.

EFFECTS OF INCONSISTENT CONVERGENCE CRITERIA

Equations of state vapor-liquid equilibrium calculations involve sets of nested iterative calculations. The use of inconsistent convergence criteria in different dew point calculation options can lead to differing dew point temperatures from the different options.

Consider the isothermal-isobaric ($T - P$) flash calculation. With fixed T , P and K_i values, Equation 5 must be solved using trial values for V , the moles of vapor per mole of feed. Newton's method often is used, with V constrained to the range $0 \leq V \leq 1$. When the change in successive iterative values of V is less than the convergence criterion $EPSV$,

$$|V_n - V_{n-1}| < EPSV \quad (11)$$

the solution V_n is accepted.

Flash calculations using Simulator No. 1 asymptotically approach $L = (1 - V) = 1.0 \times 10^{-6}$ as the temperature at 41.0 bar(a) is increased in the two phase region. When the temperature is increased 0.001°C beyond the temperature where $L = 1.0 \times 10^{-6}$, the result $L = (1 - V) = 0$

results. This indicates that the convergence criterion $EPSV = 1.0 \times 1.0^{-6}$ is used in Simulator No. 1.

Oscillations in V can occur if the criterion for convergence of fugacities, $EPSF$, is smaller than the criterion for convergence of V , $EPSV$. If in Simulator No. 1, $EPSV = 1.0 \times 1.0^{-6}$, then it is probably that $EPSF > 1.0 \times 1.0^{-6}$. With these convergence criteria, it is probable that the Simulator No. 1 $T - P$ flash predicts single phase vapor at conditions near the dew point where the use of smaller $EPSV$ and $EPSF$ would predict two phases. The differences appear to increase as the number of mixture components increases and therefore the differences can be large for natural gas mixtures containing many heavy hydrocarbons. These differences can be made significantly smaller by decreasing the various criteria for convergence such that $EPSF > EPSV > EPSD$ where $EPSF$ is no greater than 1×10^{-8} ($EPSD$ is the convergence criterion for the equation of state density algorithm). Even an IBM compatible PC using double precision allows calculation precision of approximately 1.0×10^{-13} , so the use of tighter convergence criteria certainly is feasible.

It should be noted that a search at fixed pressure for a specified value of V involves iterative values for T , so that the precision in T depends on the precision in V .

POSSIBLE CAUSES OF INCONSISTENCIES

Experience in working with the BWRS equation of state shows that even when the equation of state is capable of representing the phase behavior of a hydrocarbon mixture, the algorithms to find the solutions may fail or take many iterations to converge.

For example, the way in which the dew point temperature is searched may be totally different from the way in which the dew point pressure is searched. Likewise, the way in which lower dew point pressure is searched may be different from the way that upper dew point

pressure is searched and thus certain knowledge of where in the phase diagram the initial estimate for the search is located becomes important.

The use of K -values in the single phase has no significance. When a VLE calculation is attempted in the single phase region, a two phase assumption is made and successive iterations performed until the program determines that the condition is single phase. The algorithm has to make corrections to take a step towards the solution based on a starting point. If the initial estimates for the real K -values steps the program into single phase, it is conceivable that the algorithm won't find its way out of single phase when in fact the answer may be two phase. The use of stability analysis aids in avoiding this problem, but, as noted herein, some simulators do not use stability analysis appropriately.

K -values of heavy components are very small and thus make large contributions to the dew point calculation. This is well known and may provide partial reasons for the disagreements displayed in Tables 2 and 3. Not only are K -values of the heavier fractions very small, their mole fractions are usually very small. The division of a small number by another small number accumulated in a summation may be a source of problems depending on how it is manipulated internally in the different algorithms. The use of double precision computation and care in handling truncation precision can reduce these problems.

The slope of the vapor fraction at constant pressure as a function of temperature inside the phase envelope changes significantly with pressure. If the convergence criteria for the flash calculation are such that it doesn't consider enough significant figures, it is possible that at a particular pressure a small change in vapor fraction corresponds to a large change in temperature, thus obtaining an erroneous dew point.

Perhaps the most difficult aspect of VLE algorithm development is to make the algorithm fast, as well as robust. For this reason, various methods have been used to accelerate the direct substitution method. Unfortunately, as has been noted by Michelsen [2], some of these methods can step towards wrong answers if the initial condition or any iterative step is inappropriate. Thus, some simulators may need algorithm replacement by more robust methods.

It is difficult to determine the specific cause (or causes) of differences in dew points from different algorithms within a given simulator. Possible causes of the dew point differences noted for Simulator No. 1 are inconsistent convergence criteria and/or inconsistent use of stability analysis, but of course there could be other causes. For Simulator No. 2 the indication that stability analysis was not performed in the T-P flash calculations suggests that stability analysis is not used or is used inconsistently in simulator No. 2, potentially causing the inconsistencies noted in dew points from different algorithms.

POSSIBLE SOLUTIONS

There are two primary features of natural gas VLE calculations using equations of state that become focal points in this work. One is the necessity to use stability analysis to determine whether the natural gas composition at a given temperature-pressure is two phase or single phase according to the equation of state being used. Stability analysis provides good initial K -values for two phase conditions and can be repeated every several iterations during the search algorithm to avoid trivial solutions. The second feature is the use of algorithm convergence criteria that yield higher precision for more consistent results between different algorithm types.

CONCLUSIONS

This paper shows that there is need for improvements in contemporary process simulator equation of state vapor-liquid equilibrium algorithms. These needs have become increasingly evident for natural gases as increasing numbers of heavy hydrocarbons have been detected and included in improved gas chromatographic analysis. Because these heavy hydrocarbons have large influences on natural gas high-pressure dew points, the inconsistencies in simulator dew point algorithms noted in this paper are accentuated for these mixtures. The material presented in this paper is intended to provide a focus for the improvement of these algorithms.

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LIST OF SYMBOLS

F	vapor-liquid balance function
\overline{f}_i	fugacity of component i in mixture
i	component index
K_i	equilibrium ratio or K -value for component i
L	moles of liquid per mole of feed
N	total number of components
n	iteration index
n_i	number of moles of component i in phase
P	pressure
P_c	critical pressure
R	gas constant

R_i	iterative estimate of K_i
T	temperature
T_c	critical temperature
V	volume of phase, moles of vapor per mole of feed
V_c	critical volume per unit mass
x_i	mole fraction of component i in liquid phase
y_i	mole fraction of component i in vapor phase
z_i	mole fraction of component i in feed

GREEK LETTERS

\mathbf{r}	molar density
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SUPERSCRIPTS

L	liquid phase
V	vapor phase

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TABLE I. Natural gas stream mixture composition in kilomoles per hour and characterization parameters used for pseudo-components (C6*, etc.)

Comp.	kmol/hr	Tb (C)	MW	Rel. Dens.	Tc (C)	Pc (bar)	Vc (m3/kmol)	Acentric Factor
N2	63.19551							
CO2	1010.30263							
C1	8653.28934							
C2	182.12183							
C3	47.23891							
IC	10.85145							
nC4	10.22197							
iC5	4.37504							
nC5	2.84072							
C6*	3.74482	58.9	83.1	0.676	225.41	31.196	0.35447	0.26446
C7*	7.90547	80.7	82.3	0.819	276.13	42.936	0.28731	0.22814
C8*	2.13640	109.6	98.1	0.805	307.54	35.291	0.36231	0.28587
C9*	0.74218	137.6	112.1	0.816	337.99	31.519	0.42266	0.31578
C10*	0.41940	163.2	125	0.820	363.19	28.044	0.48924	0.34853
C11*	0.28747	185.9	141	0.829	384.83	25.792	0.54002	0.40457
C12*	0.18771	205.4	154	0.862	406.53	27.594	0.51165	0.46299
C13*	0.07497	225.3	166	0.878	428.49	26.335	0.54910	0.48756
C14*	0.03476	244.6	180	0.881	446.13	24.253	0.60537	0.51824
C15	0.01825	261.6	194	0.879	460.03	22.212	0.66754	0.54786
C16*	0.00733	278.2	209	0.879	473.87	20.468	0.73174	0.57571
C17*	0.00262	293.9	224	0.879	486.71	18.931	0.79824	0.60214
C18*	0.00088	308.6	240	0.879	498.54	17.594	0.86569	0.62704
C19*	0.00047	323.2	255	0.879	510.11	16.364	0.93760	0.65198
C20+*	<u>0.00017</u>	416.6	400	0.879	581.73	10.622	1.49789	0.82595
	10000.00000							

TABLE II. Dew Points Calculated Using Simulator No. 1

Calculation Type	Pressure, bar(a)	Calculated Dew Point, °C
Phase Envelope	41.0	52.59
Separator with V=1.0	41.0	50.17
Isothermal-Isobaric Flash	41.0	41.57

TABLE III. Dew Points Calculated Using Simulator No. 2

Calculation Type	Pressure, bar(a)	Calculated Dew Point, °C
Phase Envelope	39.93	55.00
Separator with V=1.0	39.93	42.24
Isothermal-Isobaric Flash	39.93	Unstable

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